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The mechanism of antiferromagnetism in chromium

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Abstract. It is shown that two special properties of Cr are needed to explain its antiferromagnetism. One special property is the well known sensitivity to antiferromagnetic spin-density waves due to nesting of the Fermi surface. A second new special property comes from first-principles total-energy calculations on bcc Cr, which show that, although the lowest energy state is nonmagnetic, a small expansion of the lattice brings a second-order transition into a type-I antiferromagnetic phase with rapidly rising local moments. The combined properties provide a mechanism for stabilization of the unusual antiferromagnetic ground state, since a spin-density wave which modulates the moments of the antiferromagnetic phase can be used to compensate the strain energy of the lattice expansion. This combined mechanism also explains various properties of Cr, such as the great sensitivity of the antiferromagnetism to pressure, that are otherwise puzzling.

1. Introduction

It has long been known from experiment that Cr has an unusual ground-state magnetic structure, namely an antiferromagnetic (AF) spin-density wave (SDW) in which the local moment m on each Cr atom alternates direction in successive (001) planes and is sinusoidally modulated in amplitude over about 20 bcc lattice constants. The history is discussed in detail by Fawcett [1], whose review will be the reference for experimental results. The existence of an SDW is explained theoretically [2, 3] by a special property of the Cr Fermi surface, namely a nesting property. Translation between two parts of the Fermi surface by either of two nesting vectors in k -space with wave numbers equally above and below the reciprocal lattice vector in the [001] direction brings large areas of each part of the surface to near coincidence. Hence there is a special sensitivity to the potentials which have the wave numbers of the nesting vectors and are produced by modulating the spin density. Such potentials can produce sizable interactions between the nesting parts of the Fermi surface and thereby lower the energy.

This paper shows that the SDW is a weak perturbation of an AF state of bcc Cr, and the paper is mainly a study of the magnetic structure of bcc Cr. By bcc Cr is meant that both the atomic and magnetic unit cells are bcc. In AF states the bcc cell has two atoms with opposite magnetic moments. When the SDW is present the magnetic unit cell is much larger than a bcc cell, although the atomic unit cell remains closely bcc, and the crystal will be called AF Cr or SDW Cr, but not bcc Cr.

This special property of sensitivity to particular SDWs does not prove that a SDW must be present in the AF phase in Cr or that Cr cannot have an ordinary type-I AF phase. Both these features of Cr are consequences of combining the special sensitivity to SDWs with

a second special property of Cr found by application of first-principles total-energy theory. This second special property is that although bcc Cr in equilibrium has a nonmagnetic (NM) energy minimum in which m vanishes and the AF phase does not exist, a small expansion of the lattice produces a second-order transition into a type-I AF phase. This AF phase lies below the NM phase in energy at all volumes per atom greater than the transition volume. The type-I AF phase, also called a commensurate AF phase, has up and down spins alternating on (001) planes with moments of constant magnitude.

The mechanism that produces the AF ground state of Cr uses both these special properties of bcc Cr: the lattice expands to where the type-I AF phase has a suitably large m value and that m is then modulated in an SDW of appropriate wavelength. The SDW uses the nesting property to lower the energy so much that the strain energy of lattice expansion is more than compensated and thus a second energy minimum is produced which is lower than the NM energy minimum; it will be called the SDW minimum. Hence this SDW minimum becomes the AF ground state of Cr, but it is an unusual AF state with a long magnetic unit cell. In this paper the strain energy of the required expansion is estimated and that strain energy is shown to be in reasonable agreement with a recent calculation of the energy decrease in Cr produced by an SDW [4].

This mechanism also explains a number of observations that are puzzling without it, e.g., that Mo with nesting properties like Cr does not have an AF ground state, that at the Néel temperature the volume decreases and m vanishes, that Cr has a negative coefficient of thermal expansion at low temperatures, that pressure strongly reduces the Néel temperature, that addition of Mn can produce a transition to the type-I AF phase, but addition of V produces a transition to the NM phase, and that the transition to the AF phase is feeble.

The calculations solve the Kohn–Sham (KS) equations [5] in the local spin-density approximation (LSDA), a formulation which has been quite successful in explaining magnetic phases of many metallic elements and compounds. The application to Cr requires special procedures for finding and resolving close-lying magnetic phases in the small volume range of Cr in which all the magnetic behaviour of Cr occurs. The energy scale of the NM and AF phases is shown to be much smaller than was found in previous total-energy calculations, which consequently gave strain energies too large for compensation by an SDW.

Section 2 discusses computational details, the reliability of the results and the special procedures for handling magnetic phases. Section 3 gives results for the energies and moments of the NM and AF phases and compares the results to other calculations. The discrepancy in energy scales is discussed further in sections 3.2 and 5. Section 4 gives a general plausible argument for the mechanism and discusses the other observations explained by the mechanism. Section 5 has concluding remarks about the success of this combination mechanism and the significance of this first-principles explanation of antiferromagnetism in Cr.

2. Computational details

The electronic structure of Cr is found from self-consistent solutions of the spin-polarized KS equations with the augmented spherical-wave (ASW) method [6]. The KS equations use the LSDA with the von Barth–Hedin exchange-correlation potential [7] as modified by Janak [8]. The ASW method is a fast and accurate first-principles method of solving the KS equations designed for crystals with atoms in cubic or near-cubic environments. By first-principles method we mean one that has no empirical parameters in the Hamiltonian. The calculation uses the pure KS equations without relativistic or nonlocal corrections. Such

calculations have obtained good agreement with experiment for 3d and 4d elements, but the 5d elements require relativistic corrections (results obtained with the ASW for 3d and 4d elements in both the bcc and fcc structures for each element have been collected in a review [9]): lattice constants agreed with experiment within 2% [9]; bulk moduli of NM 3d and 4d elements and also Cr and Mn agreed to within 10%, but errors for Fe, Co and Ni are 20 to 25% [9, 10]; magnetic moments of ferromagnetic (FM) Fe, Co, Ni agreed within 3% [9, 11]. The practical reason for omitting the corrections is to obtain agreement with experiment. The relativistic corrections decrease the lattice constants, which the LSDA already makes too small, and the bulk moduli are made much too large. The various nonlocal corrections overemphasize magnetism [12, 13], an important consideration for the theory of Cr. Pure KS equations without corrections have also had notable success in establishing the magnetic ground state of FeRh as a type-II AF phase [14] and in finding AF ground states in several binary Fe compounds in CsCl structure [15].

Determination of the magnetic structure of Cr presents special difficulties. At a given volume a weak AF phase very near a NM phase is sought, hence the electron distributions of two close-lying energy minima must be resolved. The two phases and the two minima actually merge at the transition volume of the second-order transition from the NM phase to the AF phase. An important aid to resolving magnetic states is to carry out the calculation with constraints that fix the total spin moment M of all the atoms in the unit cell, as well as the volume. This procedure is also called the fixed-spin-moment procedure. The total energy per atom E is found at each volume per atom V as a function of M . The value of M in the unit cell combined with the atomic numbers Z of the atoms in the unit cell fix the number of up-spin and down-spin electrons. Thus the constraint of given M on the electron distribution is easily added to the constraints of given Z values, given structure (bcc) and given volume by keeping separate densities of states for up-spin and down-spin electrons in the unit cell during the iterations to self-consistency. The minima of $E(M)$ at a given V correspond to the equilibrium magnetic phases at that volume [9, 11]. A phase at $M = 0$ is then easily separated from a ferromagnetic (FM) phase, which occurs at finite M .

However the separation of NM from FM phases is easier than the separation of NM from AF phases, because both the NM and AF phases have $M = 0$ at the given V . This latter separation is achieved by careful preparation of the initial distribution of charge and spin. Thus to find the AF phase in Cr the first step is to find the solution at the M value of the FM minimum. Then the up- and down-spin distributions on half the atoms in the unit cell are interchanged to create an initial AF distribution, which is then iterated in small steps to self-consistency. After finding the solution at $M = 0$ small changes in M around $M = 0$ are made in order to determine whether $E(0)$ is a minimum. To reduce the number of iterations and make them converge more smoothly each change of M is started with the charge and spin distribution of the previous M . If there is a minimum, and if the local moments m are finite at $M = 0$, then the AF phase has been found at the given V . The NM phase is found by using an initial distribution which has moments with the same magnitude and direction on all atoms.

This procedure for finding the AF phase did not succeed in getting close to the phase transition when the two-atom CsCl cell was used [16]. During iteration at volumes greater than the transition volume the solution in the two-atom unit cell would jump into the NM phase long before the interesting range of volume and magnetic moment per atom in the bcc Cr ground state near the transition was reached. Better results were obtained with a four-atom cell which consisted of a stack of two adjacent two-atom bcc cells along [001]; this cell was needed to find the AF phases of binary Fe compounds [15]. The larger barrier between the NM and AF solutions in the four-atom cell seems to reduce the computational

fluctuations in the iteration process. Those fluctuations can bring the charge distribution into a range which converges to the NM minimum. The first calculations with the four-atom cell [17] allowed only three atoms to have independent moments. This calculation did approach much closer to the transition volume than the calculation with the two-atom cell [16], but was only able to show that the transition from the NM phase to the AF phase occurred near the NM minimum. In the present paper, by allowing the moments of all four atoms to vary freely, subject only to the constraint on their sum, the calculation was able to show clearly that the transition volume is larger than the NM minimum.

Figure 1 illustrates $E(M)$ curves at two r_{WS} values which straddle the value of r_{WS} at which m of the AF phase attains the average observed magnitude in the SDW. The figure shows that two separate solutions can be found at each r_{WS} , each with a minimum at $M = 0$. One solution is NM with $m = 0$ at the minimum and one solution is AF with the m values plotted in figure 2. Figure 1 shows points with smooth variations of energy on the scale of tenths of a mRyd/atom, shows that the AF phase is lower in energy than the NM phase and that the energy difference rapidly gets smaller as r_{WS} decreases toward the transition value r_t at which the two phases merge. The $E_{AF}(r_{WS})$, $m(r_{WS})$, and $E_{NM}(r_{WS})$ curves shown in figures 2–4 are then obtained from the minima in the $E(M)$ curves, where r_{WS} is the Wigner–Seitz or equivalent-sphere radius of the atom.

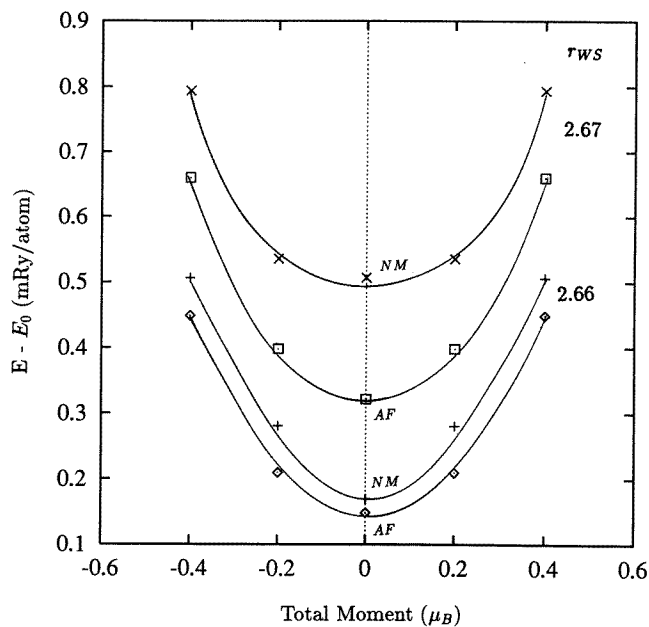


Figure 1. Energy $E - E_0$ in mRyd/atom at $r_{WS} = 2.66$ au and $r_{WS} = 2.67$ au along the AF solution branches (lower curves, marked AF), and NM solution branches (upper curves, marked NM) of the Kohn–Sham equations as functions of total moment M in Bohr magnetons in the four-atom unit cell. The phases correspond to the minima. The reference energy E_0 is the minimum energy of the NM phase at $r_{WS} = 2.645$ au. At $M = 0$ the local moment m vanishes in the NM solutions, but is finite in the AF solutions.

The properties of $E(M)$ curves are discussed at length in several papers [9, 11]. An interesting feature of such $E(M)$ curves is that the NM and AF phases corresponding to the minima are on separate solution branches of the KS equations, so that at volumes greater

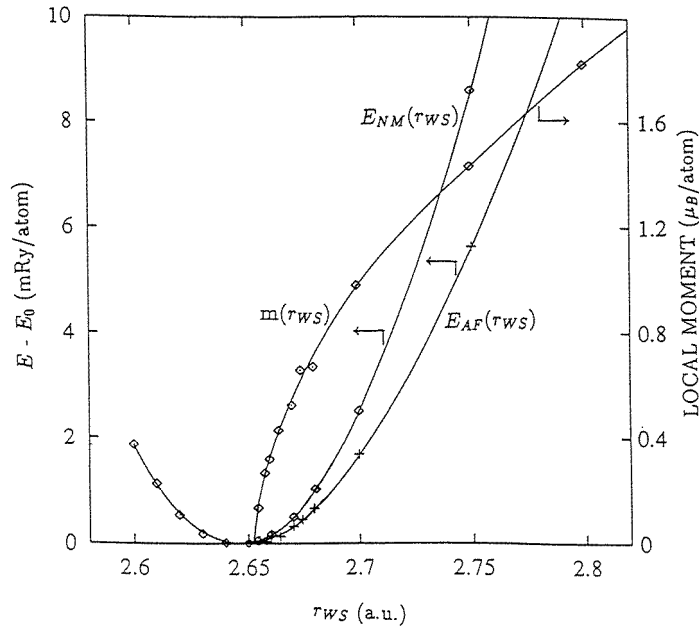


Figure 2. The total band energy of bcc Cr in the nonmagnetic state E_{NM} and the antiferromagnetic state E_{AF} in mRyd/atom as a function of the Wigner-Seitz radius r_{WS} in au (scale left) and the local magnetic moment m in Bohr magnetons per atom in the antiferromagnetic state (scale right). The reference energy E_0 is the same as in figure 1. Calculated points are shown.

than the volume of the second-order transition both phases persist, as shown in figure 2. However the NM and FM phases are on the same solution branch, hence a second-order transition from NM to FM converts the phase completely, as in bcc Fe or fcc Ni [9]. Even a first-order transition from NM to FM phase produces a two-phase range in which two minima are present for a small range of r_{WS} before one minimum and the corresponding phase is lost, as is the case for Cr [16]. The first-order NM to FM transition occurs at a lattice constant 17% higher than the NM to AF transition and the initial energy of the FM phase is 130 mRyd/atom higher in energy than the initial energy of the AF phase.

3. Results

3.1. Description of present results

Figure 2 shows the band energies in the NM and AF phases and the local magnetic moment $m(r_{WS})$ in the AF phase, all obtained from the energy minima of $E(M)$ curves like those in figure 1 at each r_{WS} used in the four-atom cell calculations. The range of r_{WS} includes the NM energy minimum at $r_{WS} = r_m$ and allows the band energies to reach 10 mRyd/atom above the minimum and m to reach $2 \mu_B/\text{atom}$. The second-order transition at $r_{WS} = r_t$ from the NM to the AF phase occurs at 0.3% expansion from r_m . Both phases continue to exist above r_t , as noted at the end of section 2.

Figure 3 plots m^2 against r_{WS} near r_t to show the linear dependence expected of a mean-field description of a second-order transition [18]. Extrapolation of the line to $m = 0$ locates the transition accurately at $r_t = 2.654$ au.

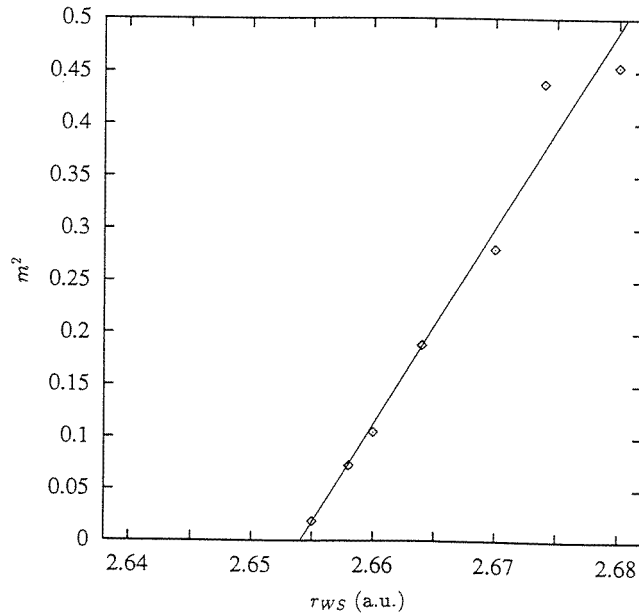


Figure 3. The square of the local moment in the AF state of Cr m^2 vs the Wigner–Seitz radius r_{WS} in a range close to the nonmagnetic to antiferromagnetic phase transition. The m^2 values are fitted to a straight line, which is extrapolated to give the value of r_{WS} at the transition $r_t = 2.654$ au.

Figure 4 expands the energy scale of figure 2 by a factor of ten and the length scale by a factor of five to exhibit clearly the NM minimum at $r_m = 2.645$ au and the start of $E_{AF}(r_{WS})$ tangent to $E_{NM}(r_{WS})$ at $r_t = 2.654$ au. Despite some scatter of about ± 0.05 mRyd/atom in the E_{AF} values near r_t , the curve $E_{AF}(r_{WS})$ is well determined by the point of tangency and the points at $r_{WS} = 2.67$ au and above. At volumes at which it exists, the AF band curve is always the ground state of bcc Cr.

In the measured SDW the mean value of m is about $0.43 \mu_B$, which corresponds in figure 2 to $r_{WS} = 2.664$ au. At $r_{WS} = 2.664$ figure 4 shows that the energy of E_{AF} is about 0.18 mRyd/atom above the minimum energy $E_{NM}(r_m)$. This strain energy from the volume expansion can be compared with the recent result by Hirai [4] that an SDW optimized with respect to wave number and moment amplitude lowers the energy of the NM phase by 0.11 mRyd/atom. Hirai's calculation is not optimized with respect to the volume per atom or to the strain wave accompanying the SDW, which would lower the energy further.

Figure 5 shows the effects on r_t and r_m of changing the electron density in Cr by varying the atomic number Z around 24. These calculations simulate the effect of adding impurities such as Mn ($Z = 25$) and V ($Z = 23$) without the effects of the disordered ion cores. Figure 5 shows that at $Z = 24.013$, which corresponds to 1.3% Mn, $r_t = r_m$ and a type-I or commensurate AF phase now exists for the alloy. Hence as Z increases above 24.013 the minimum of the NM phase now lies *above* the minimum of the AF phase, which will compete for the ground state with the SDW minimum. At 1.8% Mn a transition from the SDW minimum to the commensurate AF phase is in fact observed [1]. Figure 5 shows that m reaches $0.5 \mu_B$, the measured value of m in the commensurate AF phase, at the minimum of the energy curve at about 1.7% Mn. Figure 5 also indicates that for $Z < 24$ the transition

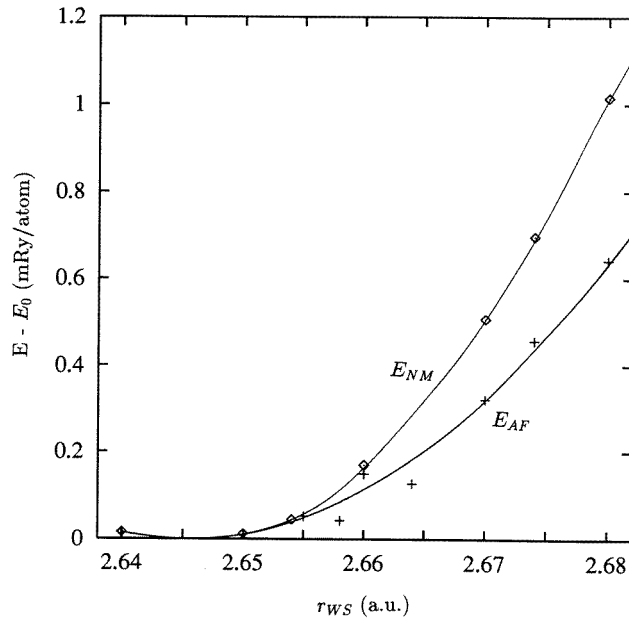


Figure 4. Total band energies $E_{NM}(r_{WS})$ and $E_{AF}(r_{WS})$ for Cr on the expanded r_{WS} scale of figure 2 that covers the minimum of E_{NM} at $r_{WS} = 2.645$ au (the reference energy) up to an r_{WS} at which m is above the value in the measured SDW. The E_{AF} curve is made tangent to E_{NM} at $r_t = 2.654$ au, the value of r_{WS} at which the phase transition to the AF phase takes place. The points at which calculations have been made are shown.

to the AF phase occurs at larger r_{WS} than at $Z = 24$, which would make the SDW less effective, since the strain energy of volume expansion is greater. Hence a transition to the NM phase is expected at some concentration of V and is in fact observed at 4% V [1].

3.2. Comparison with previous papers

The results found here may be usefully compared with the few previous calculations that found the total energy in the NM and AF phases. Kübler [19] also used the (then new) ASW method to find the total energy of the NM, AF and FM phases of bcc Cr as functions of volume. Kübler found the NM phase to have a minimum energy at bcc lattice constant $a = 2.854 \text{ \AA}$ ($r_{WS} = r_m = 2.655$ au) to be compared with the value found here of $r_m = 2.645$ au. Kübler's value includes a zero-point correction. Kübler did not find a FM phase in the r_{WS} range studied, which agrees with our result that the FM phase requires a 17% expansion of the lattice from r_m to exist [16]. However in contrast to our results Kübler found the AF phase to have a lower energy than the NM phase for bcc Cr and a finite $m = 0.59 \mu_B$ at the minimum. Kübler did not use the constrained moment procedure or a four-atom cell and used a very different procedure from the one used here for the initial distribution and calculation of the AF phase. His procedure is not described in detail and his result for the AF phase is also contradicted by the later work to be described now.

Chen, Singh and Krakauer (CSK) [20] used the general potential LAPW method with the LSDA. They included relativistic corrections and used the two-atom (CsCl) cell to find $E_{AF}(r_{WS})$ of bcc Cr for the AF phase. CSK also found no FM phase, but found $E_{AF}(r_{WS})$ for three different exchange–correlation potentials in the LSDA, including the von Barth–

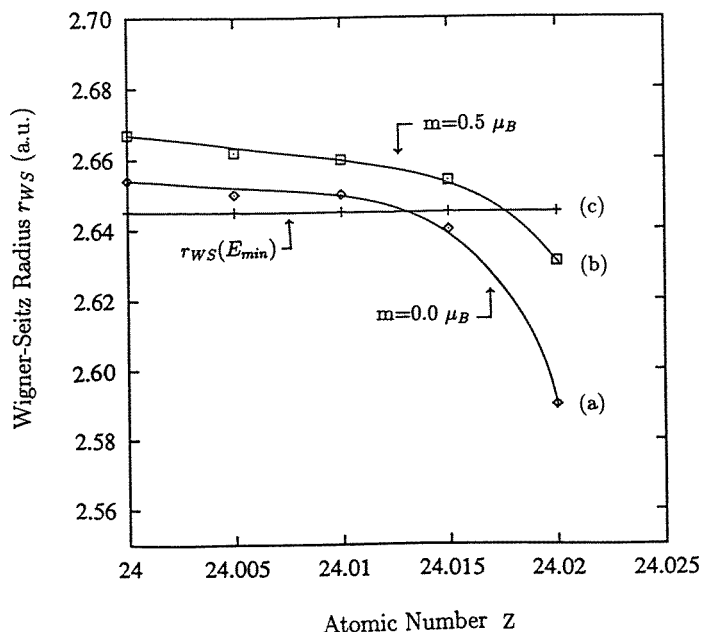


Figure 5. The variation with electron number per atom Z of: (a) r_t (calculated points \diamond), the value of r_{WS} at the transition from the NM to the AF phase; (b) the value of r_{WS} when m reaches $0.5 \mu_B$ (calculated points \square); (c) the value of r_{WS} at the minimum energy of the NM phase up to $Z = 24.013$ and then of the AF phase for $Z > 24.013$ (calculated points $+$).

Hedin form used here, which is the only one that gave reasonable results. CSK do not show $E_{NM}(r_{WS})$ separately along with $E_{AF}(r_{WS})$ and only one curve $E(r_{WS})$ is shown. Hence the transition volume is not clearly identified, but at the minimum of the one curve $a = 2.798 \text{ \AA}$ ($r_{WS} = 2.60 \text{ au}$) CSK find $m = 0$ in agreement with the present calculation and disagreement with Kübler. A value of m of $0.70 \mu_B$ is found at the experimental lattice constant $a = 2.879 \text{ \AA}$ ($r_{WS} = 2.68 \text{ au}$), which is 3% above the value of a at the minimum. More relevant would be the a value at which $m = 0.4 \mu_B$, which might be interpreted as the result of a lattice expansion like the one proposed here. However there is a serious discrepancy between their energy scale and ours; namely their energy increase from the NM minimum to the experimental lattice constant is 11 mRyd/atom, while we find 0.9 mRyd/atom. This same discrepancy appears in a later paper which repeats this Cr calculation [12], which will now be discussed.

Singh and Ashkenazi (SA) [12] repeat the LSDA calculation on bcc Cr along with two nonlocal corrections to the KS equations, all with the same von Barth–Hedin exchange–correlation. They conclude that the nonlocal corrections give magnetic effects that are too large, hence we will only consider their LSDA calculation. Again as for CSK the AF phase of bcc Cr is found to start above the NM minimum, hence the ground state is NM. Again the transition volume to the AF phase is not accurately located since their lowest value of m is $0.38 \mu_B$ in their figure 4 (the ordinate is mislabelled E). This value of m corresponds to our experience with the two-atom cell [16] mentioned above, when we also could not approach close to r_t , the r_{WS} value of the transition into the AF phase. But just as for CSK, there is a major difference in the energy scale from the calculation made here. SA find E_{AF} at $m = 0.38 \mu_B$ to be 4 mRyd/atom above the NM minimum, while we find

0.2 mRyd/atom. Since the SDW lowers energies by tenths of a mRyd/atom, the large strain energy found by SA could not be compensated by an SDW, a conclusion which they draw. However our much smaller energy differences are in the right range for such compensation.

Our previous paper on Cr with the four-atom cell, but with only three magnetic moments in the cell [17], agrees with the results here as to the general course of $E_{NM}(r_{WS})$, $E_{AF}(r_{WS})$ and $m(r_{WS})$, but is inadequate in two respects. The behaviour of $E_{AF}(r_{WS})$ was not found accurately in the critical range $r_{WS} = r_m = 2.645$ au to $r_{WS} = 2.664$ au (the expanded lattice) so that the conclusion that $r_t > r_m$ could not be drawn. Hence the paper failed to recognize that an expansion of the lattice was essential to allow the SDW to form, as is concluded here.

4. Discussion

Although the pure KS equations used here provide a consistent and reasonable first-principles description of the magnetic behaviour of Cr and other metals, quantitative modifications can be expected when reliable nonlocal corrections are available. However a persuasive qualitative argument can be given for the proposed mechanism for antiferromagnetism in Cr that should remain valid. Namely we can expect that as r_{WS} expands from r_m the NM minimum, $E_{NM}(r_{WS})$, is initially flat and the strain energy grows slowly. However above the transition point r_t , where r_{WS} has expanded by 0.3% to 2.654 au, m grows rapidly and so the size of the energy will decrease due to an SDW. Hence the decrease can be expected to overtake the slow increase of energy and stabilize an AF ground state. However the decrease is measured in tenths of a mRyd/atom, so that when r_{WS} exceeds say 2.68 au (1.3% above r_m) the strain energy exceeds 1 mRyd/atom (see figure 4) and the SDW surely can no longer compensate it, even though m is still rising. The estimate in section 2 is that a 0.7% increase from $r_m = 2.645$ au to $r_{WS} = 2.664$ au is where the rising strain energy forces the lattice to stop expanding.

Section 3.1 showed that because of the strong effects of electron density on the volume of the transition from the NM to the AF phase, the mechanism proposed here for antiferromagnetism in Cr explains the effects of adding Mn or V to Cr. Several other observations can also be explained by the same mechanism, i.e.:

(1) Although Mo has a Fermi surface with nesting properties like Cr [1, 21], it fails to have an AF ground state. This failure is readily understandable from the band structure of bcc Mo [9, 22], which shows that r_t for Mo is 17% above r_m and the strain energy at r_t is 60 mRyd/atom. However Cr, as suggested by Overhauser in 1962 [3], has ‘a fortuitously favorable band configuration’.

(2) On going up through the Néel temperature T_N Cr has a first-order transition into the disordered state with a 0.8% *decrease* in volume and the moment on the individual Cr atoms vanishes [1]. This behaviour is just what would be expected when temperature excitation breaks up the SDW leaving a strained expanded Cr lattice. The lattice will therefore shrink to the NM phase at $r_{WS} = r_m$ with no moment and with a volume decrease, which was found in section 3.1 to be 2.1%. However if we allow for the volume expansion due to zero-point vibration and thermal expansion of 0.9% (lattice parameter strain $\simeq 300^\circ \times$ average thermal expansion coefficient 10^{-5} per degree = 0.3% [1]), then the Cr relaxes at T_N by only $2.1 - 0.9 = 1.2\%$.

(3) Sections 1 and 3.1 show that Cr has two minima of energy, the NM minimum at $r_{WS} = 2.645$ au and the SDW minimum at $r_{WS} = 2.664$ au with a small barrier between them of magnitude tenths of a mRyd/atom. These two minima correspond closely to the

two phases introduced by Weiss [23] to explain the Invar effect, i.e. a negative coefficient of thermal expansion, which Cr shows at low temperatures [1]. Cr starts at 0 K in the larger-volume lower-energy minimum, but as temperature increases the smaller-volume higher-energy minimum is increasingly occupied, hence counteracts the usual thermal expansion due to anharmonic vibration.

(4) A strong effect of pressure on the effectiveness of an SDW in lowering the energy is shown in the sharp decrease of T_N with pressure found by McWhan and Rice [24]. This sharp decrease is not explained by the effect of pressure on the Fermi surface, which changes little with pressure [25]. However the mechanism proposed here predicts that pressure should strongly decrease the effectiveness of the SDW, since m decreases rapidly as r_{WS} decreases.

At high pressures the mechanism proposed here would also predict that T_N vanishes for a 1.2% decrease in volume, since the AF phase disappears below that volume. This prediction is apparently contradicted by the measurements of McWhan and Rice, who find that T_N does not vanish even at 90 kbar of pressure, which they interpret as a volume decrease of 5%. However they use a standard equation of state to convert the pressures into volume changes. If Cr had an unusually large bulk modulus at low temperatures, the actual volume change would be much smaller. Since the compressive side of the SDW minimum—from r_t up to r_{WS} at the SDW minimum—is produced by the steeply rising m values, it is plausible that SDW Cr has a large bulk modulus for compression at low temperatures. Hence the volume decrease would be smaller than estimated, and plausibly not large enough to eliminate the AF phase and the SDW at 90 kbar.

An additional argument that supports this explanation of the behaviour of Cr under high pressure is as follows. If the bulk modulus B were to stay constant under pressure p , the volume reduction ΔV would be just proportional to p . Then T_N would decrease *more* rapidly as p increases, since m decreases more rapidly as r_{WS} decreases toward r_t . Hence the observation that T_N decreases *less* rapidly as p increases and the fact that p has little effect on the nesting of the Fermi surface [25] imply that ΔV is not decreasing linearly and that B is increasing, as suggested above.

(5) The feeble nature of the ordering in the AF phase of SDW Cr has been frequently noted [1–3], but an explanation was not possible before introduction of the present mechanism. The transition to the AF phase must be called feeble, since m has values less than $0.6 \mu_B$, whereas m rises to more than $5 \mu_B$ in the AF phase when the lattice expansion is continued [9, 16]. This early cutoff of the phase transition has already been explained in this section as forced by the rapidly rising strain energy given by $E_{AF}(r_{WS})$.

5. Conclusions

The development here shows that a careful treatment of the magnetic structure of bcc Cr is valuable, a conclusion that might be expected since the AF ground state of SDW Cr is a weak perturbation of an AF state of bcc Cr. The existence and many properties of SDW Cr are successfully explained by the properties of AF bcc Cr, with its very small energy differences from the NM phase and its great sensitivity to volume near the transition volume, combined with the special sensitivity to SDW's. Fawcett has concluded [26] that 'The fundamental reason for this strong volume dependence [of the magnetic properties of the Cr system] is not known, but it seems to have little connection with the nesting of the Fermi surface'. This reason is now provided by the mechanism proposed here.

This success provides additional justification for the application of the pure KS equations to magnetic phases of metals with the LSDA, but without corrections. This success also

shows the value of the constrained moment procedure in locating and testing the stability of magnetic phases. The accurate location of the AF band has not been found without this procedure. For the difficult problem of tracing out the different phases at the second-order transition in Cr it was also necessary to use a larger unit cell than the two-atom bcc cell.

Deriving the magnetic structure of Cr from first principles is a valuable advance in the theory of Cr. Not only do the KS equations provide a well tested and well defined description of ground-state properties, but, since no parameters are required, the theory applies equally well in all situations. Thus the theory gives reliable results on the very small length and energy scales that are involved in perturbing bcc Cr to become SDW Cr.

Finally we note again the disturbingly large discrepancy between the energy scale of the magnetic phases found here and the 1992 calculation of Singh and Ashkenazi [12]. We need to find the reason for the discrepancy, since the larger energy separations would make the proposed mechanism for SDW Cr impossible and this discrepancy might appear in other calculations. One possibility is the effect of the relativistic corrections used by SA, but not in the present work.

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